CONFERENCE OF THE COMMITTEE ON DISARMAMENT

CCD/432
16 July 1974
Original: ENGLISH

LETTER DATED 12 JULY 1974 FROM THE PERMANENT REPRESENTATIVE OF FINLAND TO THE SPECIAL REPRESENTATIVE OF THE SECRETARY-GENERAL TO THE CONFERENCE OF THE COMMITTEE ON DISARMAMENT TRANSMITTING A WORKING PAPER BY THE GOVERNMENT OF FINLAND

ON METHODOLOGY FOR CHEMICAL ANALYSIS AND IDENTIFICATION OF CW AGENTS - PROGRESS OF A FINNISH RESEARCH PROJECT

Upon instructions from my Government, I have the honour to enclose a Working Paper by the Government of Finland to the Conference on Disarmament with the request that you would take appropriate steps to have it distributed in the Conference of the Committee on Disarmament.

Enclosed please find also a matrice for the printing of some illustrative figures attached to the Working Paper.

(Signed) Klaus A. Sahlgren
Permanent Representative
of Finland

GE.74-67423
74-23001

WORKING PAPER BY THE GOVERNMENT OF FINLAND TO THE CCD

Methodology for chemical analysis and identification of CW agents

- Progress of a Finnish research project

1. In 1972, the Government of Finland announced a project on creation on a national basis of a CW control capacity for possible future international use (CCD/381). This working paper noted that at least initially the work would focus mainly on organophosphate nerve agents while some work would also be done on mustards. In a subsequent working paper (CCD/412) the Finnish Government described in some detail the scientific activities connected with the project, the instrumental methods used and the laboratories engaged in this research. One of the goals of the project was to be an analytical handbook for CW verification, a compilation of standardized data for the identification of various CW agents, especially organophosphates and mustards, as well as their precursors, metabolites and degradation products.

This paper presents a more detailed description of the methods chosen and illustrates with a few examples the data obtainable by these methods. The figures included in this working paper also suggest a format for the presentation of such data for verification purposes.

2. The need for national verification activities and their international standardization has been stressed in several working papers of the CCD, e.g., the draft convention (CCD/361) and the working paper (CCD/403) submitted by the socialist states, while the need and role of international verification has been stressed, e.g., in the working paper of the non-aligned countries (CCD/400) and the recent draft convention submitted by Japan (CCD/420).

3. Among the different verification methods in the context of a CW-treaty, chemical analyses have obviously an essential role among the verification techniques. For this purpose national and international control laboratories capable of analysing previously unknown components even at ppm or ppb level in multicomponent mixtures are needed. Such requirements can be met by combining the techniques of environmental residue studies with modern methods of structure analyses. Whatever the solution of the verification question or the agreed combination of national and international means of verification, such data must be obtained by internationally agreed, standardized methods and reported in an internationally agreed, unambiguous format to fulfill the requirements of international comparability and criticality.

Concerning the nerve agents (sarin, VX etc.) the enzymatic method for detection of anticholinesterase compounds is the most sensitive indicator. If, however, there is need for more knowledge of the structure of the agent or if some other kind of CW agent (e.g., a mustard) is in question, other methods must apply. In many cases the compound to be identified is not even the agent itself but a metabolite, degradation product or precursor of it. The methods of classical chemical analysis often demand too much time or material, but the modern physical methods -- mass spectrometry, infrared spectrometry (IR), and nuclear magnetic resonance spectrometry (NMR) -- have been found more suitable.

By preparation of the samples the reactivity of the agents has to be taken into account, so that the extraction and the purification have to be made with caution, the physical methods like chromatography, ion exchange and gel filtration being the methods of choice.

In order to find out the suitability of these analytical methods in respect of CW verification, each research group engaged in the Finnish project has concentrated on the study of one of them. In addition, various organophosphorus esters, halogenides and other model compounds have been synthezised, and the kinetics of the formation and decomposition reactions have been studied.

4. In analysis of CW agents gas, liquid and thin layer cromatography are perhaps the most used methods. The detection level of a picogram may be reached using electron capture and alkali salt flame ionization detectors and also by the use of photoelectric detectors (sensitive to phosphorus and sulfur compounds). Chromatograms are suitable for quantitative evaluation when the agents in question is previously known. The identification of an unknown compound from a chromatogram peak needs more structure analytical measures; the retention time of a component alone is not a very realiable evidence.

5. At present, mass spectrometry connected to gas chromatography is the most sensitive method for structure analysis of components in an unknown mixture of organic compounds; spectra from nanogram quantities are obtainable. By using glass capillary columns in gas chromatograph-mass spectrometer also a very efficient separation of the components can be performed. Time needed for the analysis is quite short if an ON LINE computer connected to the mass spectrometer is available. As an example a spectrum of sarin is presented in Figure 1.

6. NMR spectrometry, especially the ^{13}C and ^{1}H resonances, is perhaps the most effective method for obtaining knowledge of the structure of an unknown organic compound without reference material. Concerning nerve gases, also ^{31}P and ^{19}F resonances are very valuable. The main limitation of the use of NMP in residue analyses has been the low sensitivity. The present fast progress in this field will remove part of this limitation. At present, proton and fluorine megnetic resonance spectra from microgram samples are obtained by using pulse Fourier techniques with ON LINE computer. As an example ^{1}H and ^{13}C spectra of sarin are illustrated in Figures 2 and 3.

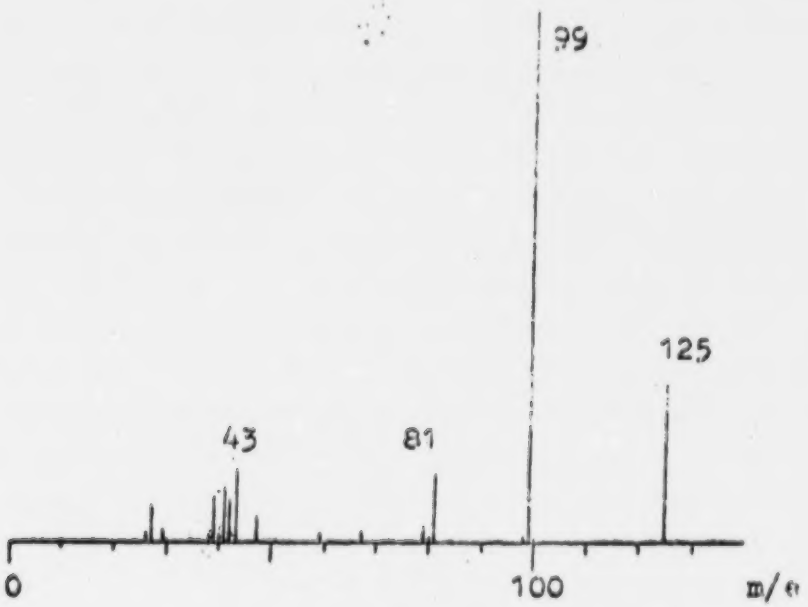
7. Infrared spectrometry (IR) is an analytical method which gives structural information about skeleton type and functional groups of previously unknown molecules. Alone it is a useful method of identification when large reference collections like the Sadtler or the Hummell & Scholl Catalogues are available. Without such collections IR often is not able to give the final structural formula but it is a fast and cheap method for fingerprint classification of unknown materials. There are now available data for over 5600 organophosphorus compounds and their empiric correlations. IR gives further straight information on the bonds of molecules in some cases where mass spectrometry and NMR spectrometry can give only secondhand information, for instance in thiono -- thiolo isomerism. It is possible to extend the sensitivity of IR spectrometry down to microgram level by using special techniques. Samples of pure components can be collected by preparative chromatography. In addition to low instrumental expenses another advantage of the infrared spectrometry is that it is also suited for the mobile laboratory purposes. In Figure 4 the IR spectrum of sarin is presented.

8. For the chemical control work it is extremely important to know how these compounds behave in different open air conditions. Therefore the Finnish project has investigated the hydrolysis and alcoholysis reactions of phosphoromono- and dichloridates after they have first been synthesized. For this purpose a quick, safe and sensitive method was developed, in which conductivity changes caused by hydrogen chloride are measured during the reaction. A model reaction is presented in Figure 5, where the shares of different components are plotted against reaction time. It is evident from the figure that the reaction rate of the chlorine atoms are not equivalent. The reaction scheme is given in the Figure, too.

In respect of the enzymatic detection method for anticholinesterase agents the toxicology-group has confirmed, using the method of Ellman, that in cases of toxification caused by organophosphorus compounds the cholinesterase activity of human blood and cerebellum is remarkably diminished and well verifiable. In animals, the cholinesterase activity of blood is too weak for realiable evaluation of alterations, whereas in small animals as rats and mice, the activity of brain (cerebrum or/and cerebellum) is sufficient for studying the effects of anticholinesterase poisons.

10. It is evident that none of the analytical methods examined will be satisfactory alone. One has to choose several of the best methods, or maybe use all of them to complement each other. In any case, however, a large collection of reference data will be very helpful even if not quite necessary. For this purpose the Finnish project has started to collect all the analytical information obtained during the work concerning chemical agents, e.g., the chromatographic and kinetic information as well as mass-, IR- and NMR-spectra of the compounds. As mentioned earlier (CCD 412/73) a handbook containing such information would be helpful for verification purposes both in its national and international aspects. It is hoped that the Finnish project will make a contribution towards that end.

Fig. 1. Mass spectrum of the nerve agent sarin with a proposed scheme for the fragmentation



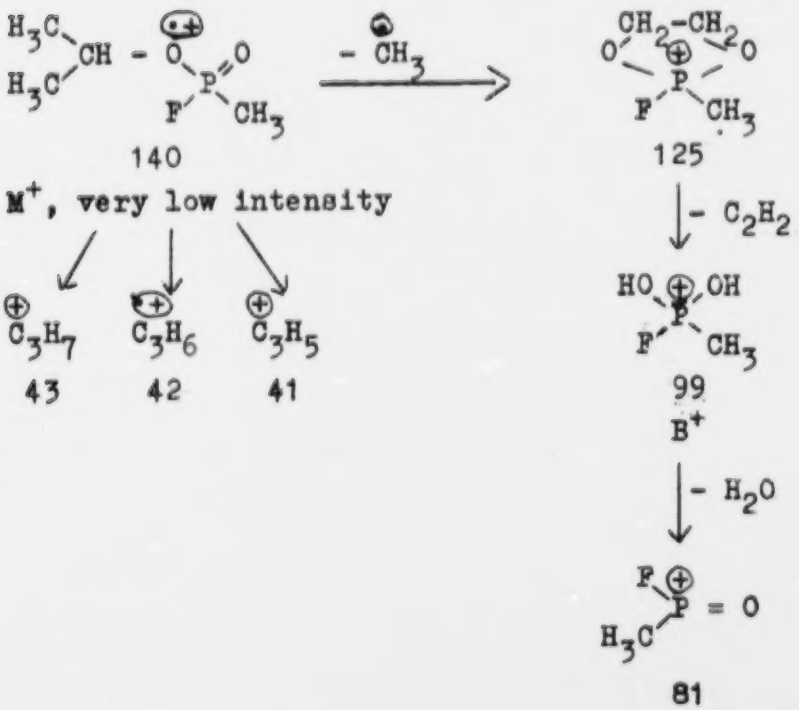


Fig. 2. ^{1}H resonance spectrum of sarin in deuterochloroform

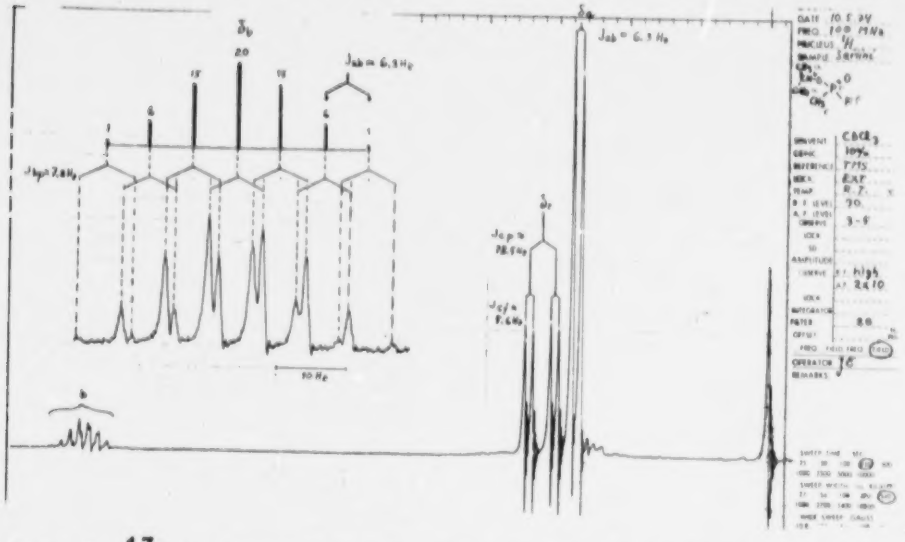


Fig. 3. ^{13}C resonance spectrum of sarin in deuterochloroform

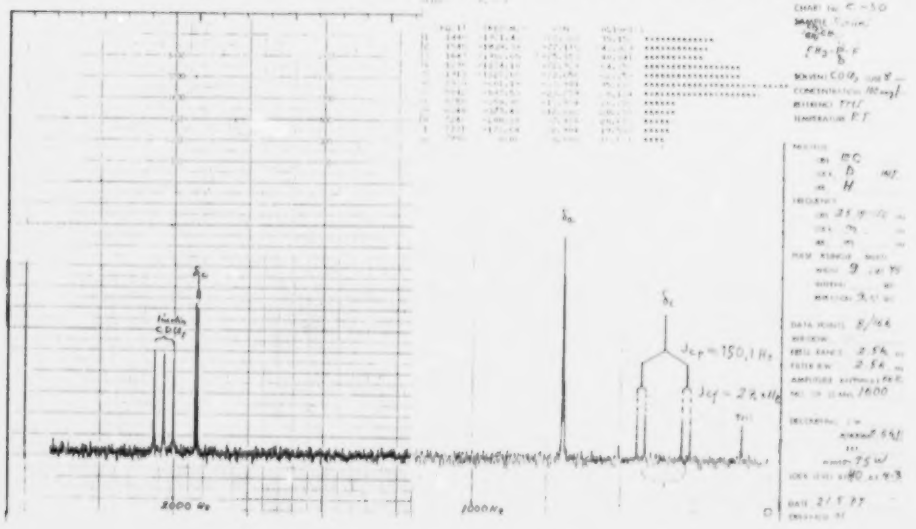


Fig. 4. Infrared spectrum of sarin, solventfree film between KBr plates

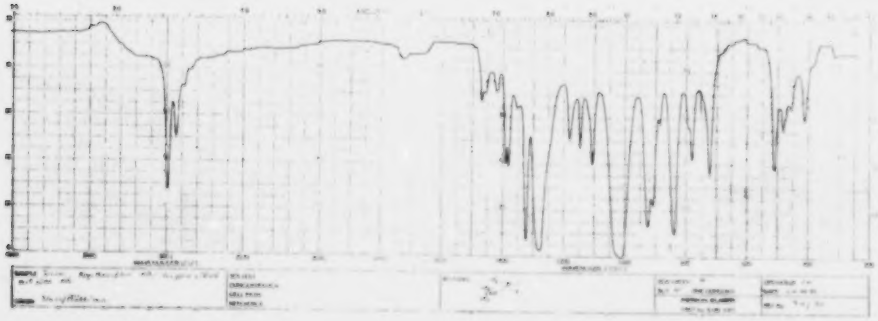


Fig. 5. Kinetics of the alcoholysis of an alkylphosphonodichloride